

Efficient synthesis of manganese(II) carboxylates: from a trinuclear cluster $[\text{Mn}_3(\text{PhCO}_2)_6(\text{THF})_4]$ to a unique $[\text{Mn}(\text{PhCO}_2)_2]_n$ chiral 3D network†

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An efficient synthetic procedure for obtaining manganese carboxylates including a trinuclear cluster $[\text{Mn}_3(\text{PhCO}_2)_6(\text{THF})_4]$ and a unique $[\text{Mn}(\text{PhCO}_2)_2]_n$ chiral 3D network is reported. The procedure involves a simple redox process, in which acidic protons are reduced to gaseous hydrogen by oxidizing metallic manganese under solvothermal conditions.

Manganese carboxylates are attracting a lot of attention due to their fundamental importance in biological systems,¹ catalysis² and materials science.^{3–5} During the last two decades, comprehensive research on homoleptic manganese carboxylate crystal engineering has been undertaken. These efforts have revealed a considerable potential to acquire 2D and 3D networks,⁴ with persistent porosity.^{4b,5} Manganese carboxylates are also invaluable in the field of molecular magnetism.⁶ Since the discovery of the first $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_x]$ cluster,⁷ a few methods to synthesize single-molecule magnets and their precursors have been developed. Most commonly, the synthetic approach is based on reacting a carboxylate precursor, typically $\text{Mn}(\text{O}_2\text{CMe})_2$, followed by a reaction with the desired ligand.⁶ Common starting materials for the synthesis of polynuclear Mn(II) carboxylates have essentially rested on a few commercially available manganese reagents. It is well known that metallic Mn reacts easily with strong mineral acids, and the same was reported for the strongest carboxylic acid, $\text{CF}_3\text{CO}_2\text{H}$ ($\text{p}K_a$ 0.23).⁸ Despite this, the reactivity of metallic manganese towards weaker carboxylic acids remains essentially undocumented. Thus, in the course of our extensive

studies on the chemistry of metal carboxylates,⁹ we attempted to develop a method that would allow efficient synthesis of highly pure Mn(II) carboxylates as starting materials for further transformation. We forced metallic manganese to react under solvothermal conditions with commercially available benzoic acid, and pivalic acid as one of the weakest carboxylic acids. The following oxidation of metallic manganese coupled with acidic proton reduction leads to formation of a Mn(II) carboxylate salt and H_2 (Scheme 1). This procedure allows the inconvenient ligand substitution step to be eliminated and simplifies the whole synthetic pathway to manganese carboxylate. To ensure the required activity of the reacting species, the reaction was performed under solvothermal conditions at 120 °C. To avoid contamination by the residual acid, a small amount of excess Mn is desired. This allowed the product to be easily isolated in high yield through crystallization without additional purification. Two types of Mn(II) benzoates, a homoleptic benzoate $[\text{Mn}(\text{PhCO}_2)_2]_n$ (**1**) and a trinuclear† THF solvate $[\text{Mn}_3(\text{PhCO}_2)_6(\text{THF})_4] \cdot \text{THF}$ (**2**·THF), and a THF solvated Mn(II) pivalate, $[\text{Mn}_6(\text{tBuCO}_2)_{12}(\text{THF})_4]_n$ (**3**), from this procedure were acquired. Note that the analogous synthesis carried out under reflux in a N_2 atmosphere causes considerable inconvenience¹⁰ and yields a contaminated product, e.g., the formation of a small amount of oxomanganese $[\text{Mn}_6\text{O}_2(\text{PhCO}_2)_{10}(\text{MeCN})_4]$ (**4**) has been often encountered (for details, see ESI†).

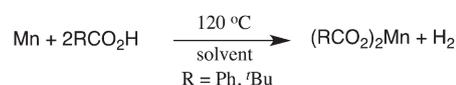
Compound **1** crystallizes as an extended chiral 3D network in an orthorhombic system, $P2_12_12$ symmetry group. The network is constructed from three different types of triangular-shaped secondary building units (SBUs) and a mononuclear node unit (MNU) (Fig. 1). There are two distinguishable connection types between SBUs, vertex sharing and MNU bridging.

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† Electronic supplementary information (ESI) available: Experimental procedures and details of the structural solutions, X-ray data for **1**, **2**, **3** and **4**. CCDC 949071, 949072, 959486 and 959487. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt53211a



Scheme 1

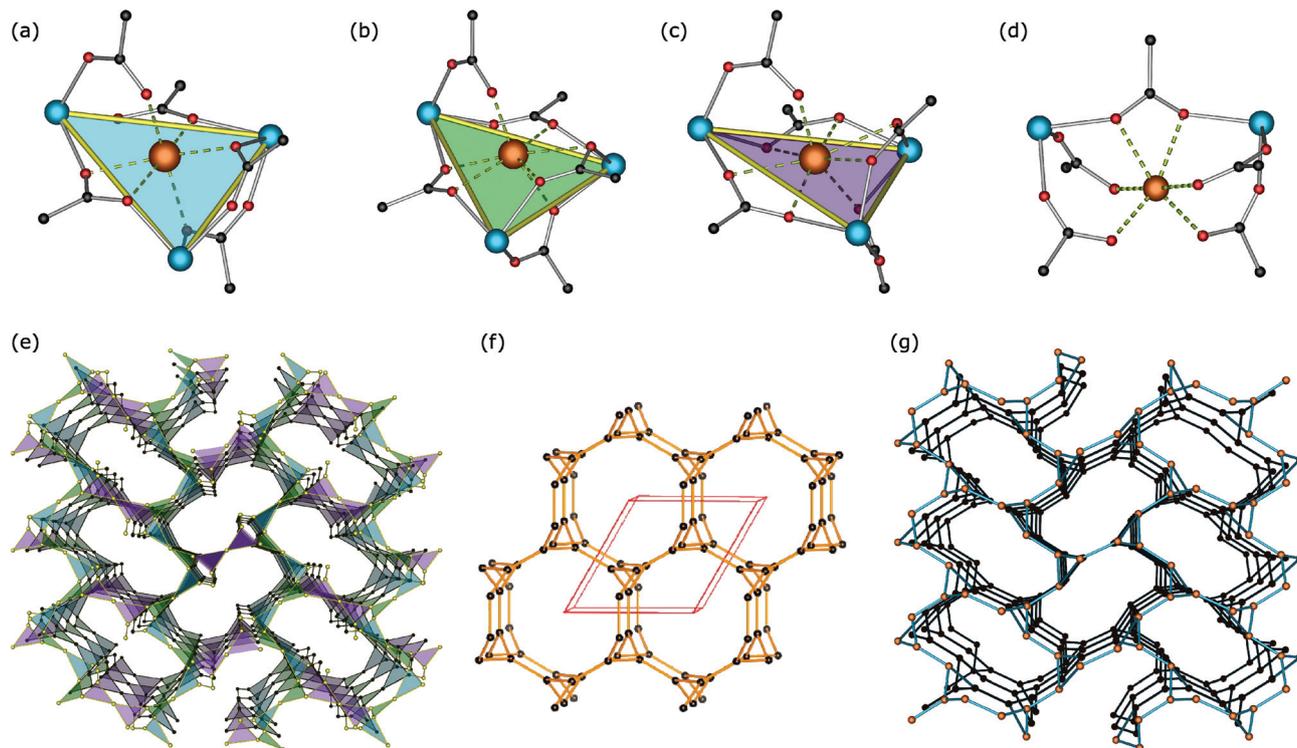


Fig. 1 Crystal structure of **1** and the corresponding building units with emphasis on the coordination sphere of the central Mn (orange) atoms: (a) blue triangle, SBU1, distorted octahedral; (b) green triangle, SBU2, distorted pentagonal bipyramidal; (c) purple triangle, SBU3, distorted hexagonal bipyramidal; and (d) MNU, octahedral. (e) Representation of the arrangement of SBUs in the crystal lattice of **1**; (f) undistorted *eta* net;^{11a} (g) topological view of the distorted *eta* network of **1** along the crystallographic *c*-axis.

Each of the SBUs is formed of tetranuclear clusters made of benzoate-bridged Mn(II) centers. In these triangles, vertices are formed by three octahedrally coordinated Mn(II) centers, while the central Mn(II) atoms adopt tetragonal bipyramidal, pentagonal bipyramidal, and rare hexagonal bipyramidal structure in SBU1, SBU2, and SBU3, respectively (Fig. 1a–d). Analysis of connectivity of this network reveals that SBU1 is connected to two SBU2 and one SBU3 through vertex sharing and MNU bridging, respectively. Similar to SBU1, SBU3 is linked with SBU2 and another SBU3 by vertex sharing, and with SBU1 through vertex sharing with two SBU1 and one SBU3; there is no MNU bridging in this case. The linking carboxylate adopts three different coordination modes, $\eta^1:\eta^1:\mu_2$, $\eta^1:\eta^2:\mu_3$, and $\eta^2:\eta^2:\mu_3$ modes, that represent both bridging and chelating interactions. It is also noteworthy that we identified SBU3 as a new type of building unit in Mn-based metal–organic frameworks. From a topological point of view, the supramolecular structure of **1** resembles an *eta* network according to the RCSR^{11a} system (Fig. 1f). The chirality of the network is not a consequence of chirality of the building units, but is derived from the *eta* net topology.¹¹ In order to determine the enantiomeric composition of bulk samples of **1**, we performed solid state CD measurements, which have shown that the product is a racemic mixture of crystals.

The solvated manganese benzoate **2** crystallizes in the form of discrete centrosymmetric $[\text{Mn}_3(\text{PhCO}_2)_6(\text{THF})_4]$ units

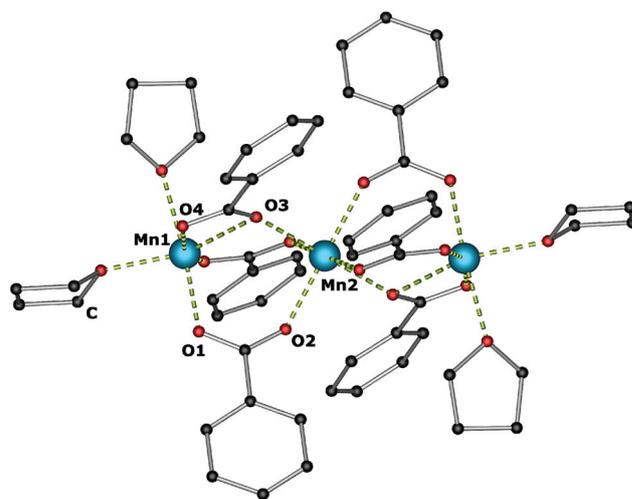


Fig. 2 Molecular structure of **2**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Mn1–Mn2, 3.5172(4); Mn1–O1, 2.290(2); Mn1–O2, 2.245(2); Mn1–O3, 2.131(2); Mn2–O2, 2.197(2); Mn2–O4, 2.139(2); Mn1–O2–Mn2, 104.70(8); O1–Mn1–O2, 58.02(7).

(Fig. 2). It has a linear chain arrangement with Mn(II) centers bridged by two $\mu_2(\eta^1,\eta^1)$ -benzoates and one $\mu_2(\eta^1,\eta^2)$ -benzoate. The geometry of the central ion is almost perfectly octahedral, while the coordination spheres of terminal Mn atoms exhibit considerable angular distortion, particularly where the

$\mu_2(\eta^1, \eta^2)$ environment of the terminal metal centers is completed by THF molecules. Molecules of **2** are subject to weak intermolecular C–H $\cdots\pi$ interactions, which influence their mutual orientation at low temperatures. Compound **3** crystallizes as a 1D coordination polymer in a triclinic system, $P\bar{1}$ symmetry group. Manganese centers are bridged by a total of twelve BuCO_2^- ligands in four different coordination modes: $\eta^1:\eta^1:\mu_2$, $\eta^2:\eta^1:\mu_2$, $\eta^2:\eta^1:\mu_3$, and $\eta^2:\eta^2:\mu_3$. The remaining coordination sites are occupied by four terminally coordinated molecules of THF (for details, see ESI†).

The temperature dependences of the susceptibility for **1** and **2** are shown as χT vs. T plots in Fig. 3, and magnetization curves at 2 K are shown in the inset (for **3**, see ESI†). The $\chi T(T)$ dependences indicate the overall antiferromagnetic (AF) behavior of both compounds at low temperatures and paramagnetism at high temperatures. The $1/\chi$ vs. T plots for **1** and **2** are linear in the range of 35–300 K and $\chi(T)$ curves can be well described by a Curie–Weiss function with the following values: $C = 4.25$ and 4.5 , $\theta = -31.4$ K and -19.9 K for **1** and **2**, respectively. The obtained C values are close to 4.37, which is the value expected for magnetically isolated Mn(II) ions. The magnetization curve of **1** measured at 2 K reveals no hysteresis and is linear in the high field region ($H > 4$ T). The effective magnetic moment per Mn ion at 9 T is $1.56\mu_B/\text{Mn}$, which is too small to be ascribed to uncoupled $S = 5/2$ spins. The $M(H)$ behavior and obtained θ value of -31.4 K indicate that there is appreciable AF coupling between the magnetic centers in **1**. Although all manganese ions are bridged with comparable Mn–Mn distances (3.187–3.629 Å), there is no sign of a transition to long-range magnetic ordering down to 2 K. This means that either the inter-Mn couplings are not strong enough to stabilize a 3D magnetic structure or other factors

preclude the transition into a collective magnetic state. For tetranuclear clusters made of benzoate-bridged Mn(II) centers with the triangular shape (Fig. 1) it is expected that Mn–Mn antiferromagnetic interactions give rise to a spin frustration among Mn spins that, as a rule, shifts the magnetic ordering transition to lower temperatures. The $\chi(T)$ dependence of **2** could be reproduced using solutions of a spin Hamiltonian for the trimer with a linear arrangement of spins $S_1-S_2-S_3$ ($S_1 = S_2 = S_3 = 5/2$, $J_{12} = J_{23} = J$).¹² The theoretical curve matches the experimental data in the whole temperature range for $J = -1.99$ cm^{-1} , $J_{13} = -0.7$ cm^{-1} , $zJ' = -0.12$ cm^{-1} , and $g = 2$ with the agreement factor $R = 3.4 \times 10^{-4}$ (zJ' is an intercenter interaction parameter). The coupling constant J obtained with this model is comparable to the results reported for Mn_3 systems with similar topology ($J \sim -1.4$ to -2.8 cm^{-1}).¹³ This relatively small value leads to a close spacing (of a few cm^{-1}) of the ground and first excited spin states. The partial population of the excited state at small fields and the spin state crossover at higher fields explain the non-Brillouin behavior of the magnetization curve at 2 K.^{12a,13b}

Conclusions

In conclusion, a new convenient one-pot synthetic procedure to prepare anhydrous manganese carboxylates was developed. The product composition and structure may be controlled by the choice of solvent.

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Notes and references

† Crystal data for **1**; $\text{C}_{280}\text{H}_{200}\text{Mn}_{19}\text{O}_{80}$; $M = 5888.26$, crystal dimensions $0.48 \times 0.32 \times 0.28$ mm^3 , orthorhombic, space group $P2_12_12$ (no. 18), $a = 38.8251(2)$ Å, $b = 17.6702(2)$ Å, $c = 19.4001(5)$ Å, $\beta = 117.427(2)^\circ$, $U = 13309.1(4)$ Å³, $Z = 2$, $F(000) = 5990$, $D_c = 1.469$ g m^{-3} , $T = 100(2)$ K, $\mu(\text{Mo-K}\alpha) = 0.952$ mm^{-1} , $\theta_{\text{max}} = 27.49^\circ$, $R_1 = 0.0768$, $wR_2 = 0.1549$ for 27733 reflections with $I_o > 2\sigma(I_o)$. CCDC 949071.

Crystal data for **2**; $\text{C}_{124}\text{H}_{143}\text{Mn}_6\text{O}_{34}$; $M = 2507.02$, crystal dimensions $0.38 \times 0.30 \times 0.26$ mm^3 , triclinic, space group $P\bar{1}$ (no. 2), $a = 11.4356(3)$ Å, $b = 12.0816(2)$ Å, $c = 21.5601(5)$ Å, $\alpha = 85.3518(12)^\circ$, $\beta = 89.0215(12)^\circ$, $\gamma = 82.4410(14)^\circ$, $U = 2943.28(11)$ Å³, $Z = 1$, $F(000) = 1309$, $D_c = 1.444$ g m^{-3} , $T = 100(2)$ K, $\mu(\text{Mo-K}\alpha) = 0.705$ mm^{-1} , $\theta_{\text{max}} = 24.71^\circ$, $R_1 = 0.0450$, $wR_2 = 0.0971$ for 8556 reflections with $I_o > 2\sigma(I_o)$. CCDC 949072.

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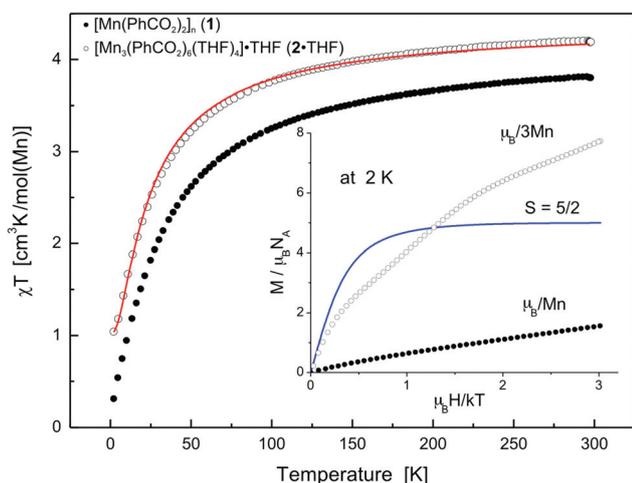


Fig. 3 Plot of χT vs. T for **1** (solid circles) and **2** (open circles). Both experimental curves (measured at 0.1 T) are presented in $\text{cm}^3 \text{K mol}^{-1}$ (Mn). The solid curve is the theoretical fit of $\chi(T)$ dependence for compound **2** (see text). Inset: magnetization curves measured at 2 K for **1** (in μ_B/Mn vs. $\mu_B H/kT$) and **2** (in $\mu_B/3\text{Mn}$ vs. $\mu_B H/kT$). The solid line is the theoretical Brillouin function for $S = 5/2$ and $g = 2$.

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